PHYSICAL REVIEW B VOLUME 47, NUMBER 13 1 APRIL 1993-I

Elastic properties of $Bi_2Sr_2CaCu_2O_x$ whiskers

R. L. Jacobsen, T. M. Tritt, A. C. Ehrlich, and D. J. Gillespie
Materials Physics Branch, Naval Research Laboratory, Washington, D.C. 20375
(Received 14 August 1992; revised manuscript received 26 October 1992)

This study reports vibrating-reed measurements of Young's modulus and internal friction made as a function of temperature, from 50–400 K, on single-crystal whiskers of $Bi_2Sr_2CaCu_2O_x$ with $T_c \approx 75$ K. The modulus along **a** is found to be lower than any earlier reported value for this material. Comparisons are made to results of previous work conducted by different methods and on platelet samples with higher T_c.

I. INTRODUCTION

The high-temperature superconductor, $Bi_2Sr_2CaCu_2O_x$, has attracted recent attention because of its numerous interesting elastic phenomena. Vibrating-reed measurements on platelets have revealed a small anomaly in the sound velocity at the superconducting transition and several unexplained internal friction peaks have been observed at temperatures of 145, 225, and 285 K, along with associated variations in the Young's modulus.[1,2] Ultrasound studies on larger crystals and polycrystals have shown a variety of other, possibly related, attenuation peaks.[3,4] Static stress measurements on whiskers show a large elastic region and provide evidence for a ferroelastic phase transition in the range from 270 to 330 K.[5] In addition, this crystal phase has for some time been known to possess intrinsic strain caused by an incommensurate modulation along its **b** crystallographic direction.[6–8]

This study reports investigations using the vibrating-reed technique on whiskers of this material with a superconducting transition temperature of about 75 K. Comparisons are made to results of previous work on samples with higher T_c, and the temperature range of observations is extended up to 400 K.

II. EXPERIMENTAL TECHNIQUE

Our samples are whiskers of $Bi_2Sr_2CaCu_2O_x$, which were grown by a powder sintering process described elsewhere.[9] Two separate batches of whiskers were provided to us, one by Jung and Franck, the other by Marone. Typical dimensions of a whisker are $1000\times20\times2$ μm^3. The growth direction lies parallel to the **a** axis, whereas the shortest dimension is parallel to the **c** axis.[10] The whiskers are single crystal and have been identified as having a superconducting transition temperature of 75 K by Jung and Franck.[9]

Our measurements were made with the vibrating-reed technique. Each specimen was affixed to a mount in a cantilever configuration (i.e., one end free) with a drop of silver paint. The mechanical resonance frequencies and width of each resonance were then determined. For a vibrating bar, Young's modulus Y and resonant frequency f_r are related by

$$Y=(\alpha^2 l^4 \rho/t^2) f_r^2 , \tag{1}$$

where l is the sample length, t the thickness, and ρ the density (about 6.7 g/cm^3 for $Bi_2Sr_2CaCu_2O_x$). The constant α, is determined by the boundary conditions and mode of vibration, and by the shape of the whisker's cross section. For fixed-end/free-end boundary conditions, the fundamental mode, and a rectangular cross section, $\alpha \approx 6.2$ (Ref. 11). The internal friction, a measure of the rate of energy dissipation during vibration, is the inverse of the quality factor and can be determined from the width of the resonance at the half-power points Δf (Ref. 12):

$$1/Q=\Delta f/f_r . \tag{2}$$

Note that because the long direction of our whiskers corresponds to the **a** axis, we are measuring the modulus along that direction exclusively, and not a combination of **a**- and **b**-direction moduli as reported by others who have worked on platelet samples.

III. RESULTS AND DISCUSSION

We find the magnitude of the Young's modulus to be quite low in these whiskers. It is difficult to obtain very accurate values for absolute moduli due to uncertainties in both the measurement of the very small sample dimensions and the uniformity of these dimensions over the entire sample length. However, the results of Eq. (1) are certainly good to better than half an order of magnitude. All whiskers we have checked (a total of six) have given a modulus between 3 and 10 GPa. This is lower than all previously reported values for the modulus in this material. Nes *et al.* have observed moduli of 70 and 30 GPa by vibrating-reed measurements on platelets,[1,2] while Tritt *et al.* have used a static pulling technique to find a modulus of 5–20 GPa on the same whiskers used for this study.[13]

In the platelet studies, no effort was made to determine the orientation of the **a** and **b** axes, and thus those moduli represent uncertain mixtures of the elastic constants along these two directions S_{ij}. Our finding that the modulus is very low along **a** suggests that the 30 GPa platelet result is probably due primarily to S_{11} and the 70 GPa result to S_{22}. It would be useful to repeat the platelet measurements on oriented samples to verify this conclusion. If correct, this is an unusually large difference in elastic constant between two directions that are very similar crystallographically ($a=5.41$ Å, $b=5.42$ Å). Furthermore, it seems to run counter to ultrasonic data[4] that indicate the moduli in the two directions to be both roughly equivalent and greater than 100 GPa, much higher than the vibrating-reed finding.

It is possible that this situation could be accounted for by the existence of antiphase domains, first reported by Fung *et al.*[14] These planes of abrupt mismatch between lines of atoms occur only perpendicular to **a**, and could be a source of mechanical relaxation. This relaxation manifests itself as a reduced modulus, provided the applied stress is both low enough in frequency to allow time for relaxation to occur, and polarized in a direction that can drive the relaxing entity. A specific relaxation mechanism could, for example, involve motion of oxygen atoms at the antiphase boundary induced by stress or gradients in the stress. Vibrating-reed experiments have so far only been performed on $Bi_2Sr_2CaCu_2O_x$ at low frequencies, below 10 kHz, which may allow relaxation. Ultrasound, on the other hand, has not been tried below 5 MHz which may be too quick. Measurements in the frequency range from 10 kHz to 1 MHz, could confirm or deny this hypothesis if a monotonic increase on a modulus was observed along with a peak in internal friction.

The discrepancy between vibrating-reed and the static measurements does not appear very great, but if real, it may be related to the fact that the static method makes its measurements at much larger values of strain (about 1% as compared with 0.001%). It may be possible that there is a mechanism that absorbs stress easily at low strain, but which saturates at high strain, such as readjustment of the incommensurate superlattice.

We have measured resonant frequency and internal friction (under diffusion pump vacuum) as a function of temperature. Our findings are as follows.

Consistent with earlier reports, we observe no softening in modulus or feature in the internal friction at the superconducting phase transition. Unfortunately these data were not precise enough to allow investigation of the possibility of a discontinuity in the logarithmic derivative of the resonant frequency as others have seen.[1,2]

We observe the peak in internal friction at 145 K (Fig. 1). Nes *et al.* first reported this feature for samples with T_c of 93.2 and 83.8 K, and conjectured that since the temperature of the peak did not depend on T_c, it was probably not related to the superconducting transition.[1] This measurement on a specimen with T_c of 75 K further supports this hypothesis.

This peak is usually accompanied by a steeper slope of the resonant frequency with respect to temperature in the vicinity of the peak. This feature resembles the step change in modulus that is characteristic of Debye relaxation.[15] To investigate this possibility we subtracted an extrapolated background from both the frequency and friction data,[16] then normalized the data to represent the real and imaginary parts of the modulus (Fig. 2). Plotted in this way, the change in Re(Y) from one side of the peak to the other would be equal to twice the peak height of Im(Y) if a single Debye process were at work. We conclude that the change in modulus is probably too great to be explained in this manner, even for a distribution of relaxation rates.[17]

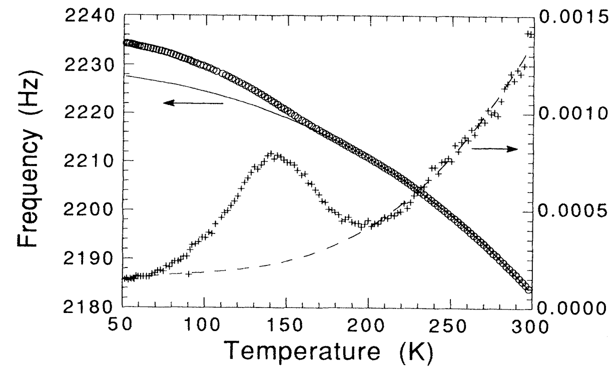

FIG. 1. Resonant frequency and internal friction as a function of temperature in whisker No. 4; solid line is a fourth-order fit to the frequency behavior well above 145 K; dashed line is the fourth-order fit to friction behavior on either side of the 145 K peak.

In two samples we have seen a decrease in the frequency near the 145 K friction peak (Fig. 3). The size of this effect decreases as the frequency of the mode observed increases.

It is possible that the frequency behavior near 145 K, shown in Figs. 1 and 3, are the result of a localized dip in modulus (perhaps associated with a displacive phase transition, as suggested by Wang *et al.*),[4] but that in only a few samples is the behavior strong enough to overcome the strong monotonic trend of the background. However, in this case it is difficult to understand why the size of the dip varies with the mode, or why the modulus does not recover to the same level below the transition for all modes.

In the authors' view, the modulus behavior in Fig. 1

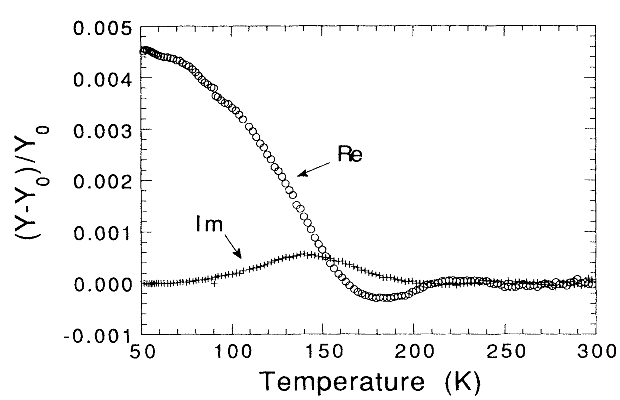

FIG. 2. Real and imaginary parts of the modulus anomaly at 145 K. The increase in the real part would only be twice the peak height of the imaginary part for a single Debye relaxation process.

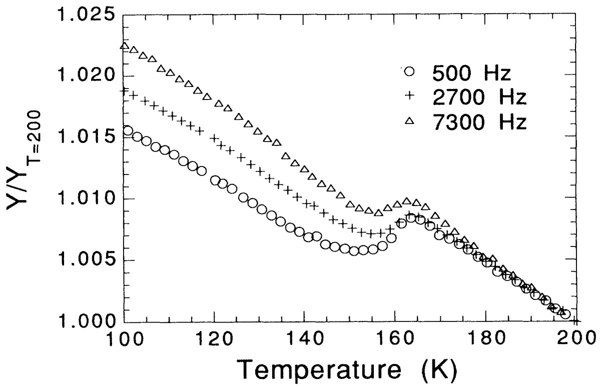

FIG. 3. Modulus, normalized to its value at 200 K, as a function of temperature for three different resonances on whisker No. 11.

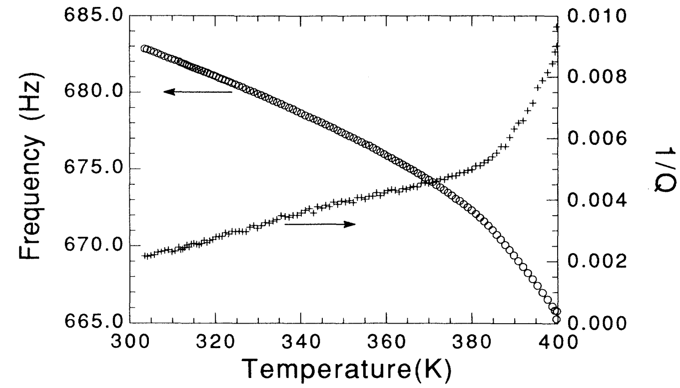

FIG. 4. Resonant frequency vs temperature on whisker No. 5.

below 150 K looks like a monotonic increase above the background with the shape of an order parameter, while that of Fig. 3 appears to be a (smeared out) downward step. These two types of behaviors correspond to two distinct coupling interactions between strain and order parameter (OP), as discussed by Rehwald.[18] The source of these two different behaviors is uncertain. However, the ultrasound work showed two different behaviors based on the direction of sound propagation.[4] Therefore it is possible that, whereas all whiskers that have so far been checked have been found to grow along **a**[5,10] the whiskers which exhibit a downward jump may have, all or in part, grown along **b**. (90° twist boundaries that reverse the orientation of **a** and **b** have been observed in $Bi_2Sr_2CaCu_2O_x$.[19]) In this case the mode dependence of the size of the discontinuity could be due to sample inhomogeneity, as portions of the reed near vibrational nodes will make less of a contribution to the net modulus.

We have also observed the internal friction peak previously reported near 225 K.[1,2] However, it often exhibited great hysteresis, being large during warming, but small or nonexistent during cooling. Wang *et al.* also reported some hysteresis in their ultrasound data in this temperature range.[4]

We observed no obvious friction peak near 280 K. Nes *et al.* noted that this peak was less visible in their lower T_c sample.[1] As the T_c of these whiskers is lower still, its absence further establishes this trend.

No unusual features were observed in the vicinity of the proposed displacive phase transition.[5] The measurements that detected the transition, while performed on whiskers from the same batches that we studied, were made at large static stresses, relative to those in vibrating reeds, and the behavior observed was characterized by a time constant of several seconds. The reported effects may be stress induced.

On one whisker we extended our investigation upward to 400 K (Fig. 4). The frequency continued to curve downward, while the friction increased linearly up to 380 K. Above this temperature the friction began to climb much more rapidly, and the frequency curves sharply downward. The cause of this behavior is not yet understood.

IV. CONCLUSION

Whiskers of $Bi_2Sr_2CaCu_2O_x$ appear to have a lower Young's modulus than that reported for platelet samples. We speculate that the lattice is soft along **a**, the direction in which the whiskers grow, and believe that varying reports on the size of the modulus in platelets are caused by a failure to orient them in a specific direction. The source of the softness along **a** may be mechanical relaxation at antiphase boundaries. Observations of various internal friction peaks in this $T_c \approx 75$ K sample have been compared with similar observations in higher-T_c platelets, helping to establish trends implicit in that data. Above 380 K, a strong upturn in internal friction has been observed.

ACKNOWLEDGMENTS

The authors would like to thank J. Jung and J. P. Franck, of the University of Alberta, as well as M. Marone and M. J. Skove of Clemson University, for providing the whiskers for this study, and George Mozurkewich for facilitating part of this work. R. L. J. acknowledges financial support from the NRC.

[1] O. M. Nes *et al.*, Physica C **185-189**, 1391 (1991).
[2] O.-M. Nes *et al.*, Supercond. Sci. Technol. **4**, S388 (1991).
[3] Y.-N. Wang *et al.*, Physica C **162-164**, 454 (1989).
[4] Y.-N. Wang *et al.*, Phys. Rev. B **41**, 8981 (1990).
[5] T. M. Tritt *et al.*, Phys. Rev. Lett. **68**, 2531 (1992).
[6] Y. Gao *et al.*, Science **241**, 954 (1988).
[7] M. D. Kirk *et al.*, Science **242**, 1673 (1988).
[8] C. Patterson *et al.*, Supercond. Sci. Technol. **3**, 297 (1990).
[9] J. Jung *et al.*, Physica C **156**, 494 (1988).
[10] J. Jung *et al.*, Jpn. J. Appl. Phys. **28**, L1182 (1989).

[11]P. M. Morse, *Vibration and Sound* (AIP, New York, 1976), pp. 151–162.
[12]J. B. Marion, *Classical Dynamics of Particles and Systems,* 2nd ed. (Academic, New York, 1970), p. 121.
[13]T. M. Tritt *et al.*, Physica C **178**, 296 (1991).
[14]K. K. Fung *et al.*, J. Phys. Condens. Matter **1**, 317 (1989).
[15]A. S. Nowick, and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972), pp. 52–57.
[16]The exact choice for the form of the background for $1/Q$ vs T is not critical and will not greatly affect the resultant peak height, so we simply used the best fit fourth-order polynomial to the data above 200 and below 70 K. The background of f_r vs T is more uncertain, and the specific form chosen can greatly affect the size of the alleged modulus step. We used the best fit to the data above 200 K of a polynomial including only second- and fourth-order terms in T, as per Alers.
[17]Nowick and Berry discuss continuous relaxation spectra on pp. 77–114, and plot the friction peak heights produced for various distributions of relaxation time on p. 104. Peak heights are generally in the vicinity of 30% of the normalized modulus change, whereas Fig. 2 shows a peak height of about 10% of modulus change.
[18]W. Reywald, Adv. Phys. **22**, 721 (1973).
[19]C. H. Chen, in *Physical Properties of High Temperature Superconductors II,* edited by D. M. Ginsberg (World Scientific, Teaneck, New Jersey, 1990), p. 248–252.